United States Patent Office 3,403,608 Patented Oct. 1, 1968

3,403,608

WATERPROOFING OF POROUS SILICIOUS MATERIALS

Clarence N. Impola, Prior Lake, and Robert H. Leitheiser, Minneapolis, Minn., assignors to Ashland Oil & Refining Company, Ashland, Ky., a corporation of Kentucky

No Drawing. Filed Sept. 14, 1966, Ser. No. 579,192
27 Claims. (Cl. 94—25)

ABSTRACT OF THE DISCLOSURE

A method for rendering a porous silicious material, such as soil, water-repellant by contacting the material with water-repelling amounts of a mono-isocyanate of the formula:

R—NCO

wherein R is a monovalent hydrocarbon radical of 6 to 32 carbon atoms. The method of the present invention can be used to create roadbeds from soil.

DISCLOSURE

This invention relates to the waterproofing of porous silicious materials such as soil by the use of chemical compounds.

Most naturally occurring soils when sufficiently compressed are capable of serving as vehicle-bearing roads or runways. Such roads and runways, because of their ease of construction may advantageously be used in areas where modern, conventional, concrete or asphalt-surfaced roads are either too expensive or require too long a construction period, e.g., roads of naturally occurring soils, which are ancient in history, are frequently used today in connection with agricultural or military operations. However, the usefulness of such roads is often limited due, among other things, to the fact that the soil of which the roads are constructed is not immune to the effects of water such as rain, floods, hail, or snow. Water usually renders the road muddy and slippery, necessitating a consequent reduction in the speed at which vehicles and personnel can safely travel and finally, in the extreme, rendering the road impassable. Consequently a method of and a material for waterproofing soil to render it immune to the effects of water has long been sought.

Accordingly, it is an object of this invention to provide an efficient and economical method of waterproofing porous silicious material. Other objects and advantages of this will appear from the following description.

It has now been discovered that soil may be rendered water-repellent by contacting it with relatively small amounts of isocyanates of the formula:

R—NCO

wherein R is a monovalent hydrocarbon radical of 6 to 32 and preferably of 12 to 24 carbon atoms. The preferred hydrocarbons are the aliphatics and the preferred isocyanates are the mono-isocyanates.

The aliphatic mono-isocyanates, which may be employed in the present invention include paraffinic and olefinic isocyanates of 6 to 32 and preferably of 12 to 24 carbon atoms. They can be straight chain or branched and the isocyanate group can be attached to a primary, a secondary, or a tertiary carbon atom. The olefinic isocyanates can be mono or poly unsaturated.

The cycloaliphatic isocyanates include among others cyclohexyl isocyanate, and substituted cyclohexyl isocyanates.

The aromatic isocyanates include among others phenyl isocyanate and substituted phenyl isocyanates.

The aliphatic aromatic isocyanates include among others phenyl methyl isocyanate and p-ethyl phenyl isocyanate. The isocyanates can contain non-reactive substituents, i.e., non-reactive with the isocyanate group and the porous silicious material to which the isocyanate is added. Specific examples of such substituents include chlorinated and nitrated isocyanates which do not significantly alter the hydrocarbon nature of the isocyanate and which contain not more than one substituent per carbon atom of the isocyanate.

Specific examples of preferred isocyanates that can be used to practice the present invention include hexyl isocyanate, heptyl isocyanate, octadecyl isocyanate, docosyl isocyanate, deceneyl isocyanate, tetracoseneylisocyanate, 2-ethyl-hexyl-isocyanate, 4-chloro-octadecyl-isocyanate, tert - 1,1-methyl-eicosyl-1-isocyanate,6-nitro-10-ethyl - 12 - bromo - isocyanate,3-hexyl-cyclohexyl-isocyanate.

In the practice of the present invention, it has been found that a variety of methods may be employed to contact the soil with the isocyanates of the present invention. For example, the soil may be removed from the surface of the earth and mixed with the isocyanates and then reapplied to the surface of the earth. Alternatively, the isocyanates may be sprayed directly or as a solution in a compatible solvent onto the soil comprising the surface of the earth.

The isocyanates of the present invention may be applied to bone dry soil, moist soil, or wet soil. When the isocyanates are applied to dry soil, the resultant composition exhibits some water-repellent characteristics. When waterdrops are applied to the surface of the bone dry soil, they wet the surface slightly. Within a few minutes of continued application the drops cease to penetrate the surface; the soil, thus, exhibiting increased water-resistance. It is to be understood that the terms dry, moist and wet are relative to the amount of water the soil can hold. For example sand containing 10% by weight of water is commonly termed wet whereas clay containing an equivalent amount of water would be termed only moist.

In one embodiment of the present invention the soil to be waterproofed can be treated with a monomer having active hydrogen atoms such as water, alcohols, amines, and the treatment may take place either before or after the application of the mono-isocyanate. In a preferred embodiment, the monomer having active hydrogen atoms is applied first followed by the application of the mono-isocyanate. The preferred monomers include alcohols and especially the glycols such as ethylene glycol which is preferred.

In still another embodiment of the present invention, the soil may be treated with a polymer having active hydrogen atoms. As in the case with the monomer, the polymer may be applied either before or after treatment of the soil with the mono-isocyanate. In a preferred embodiment, the soil is first treated with the polymer and then treated with the mono-isocyanate. Desirable polymers include homopolymers and interpolymers of the following monomers: alcohols, such as propoxylated glycols, glycerine, glucocides and amines such as diethylene triamine. Polyethers can also be employed. The most preferred polymer is propoxylated glycol.

When the mono-isocyanates are applied in solution, the solution may advantageously contain catalytic amounts such as 0.001% to 5% and preferably 0.5% to 2% of catalysts such as dibutyl tin diacetate, stannous octoate, or triethyl amine.

The mono-isocyanates employed in the present invention can be sprayed on or mixed with the soil to be treated alone or in solution with any compatible solvent. Compatible solvents are those which contain no active hy-

drogen as for example, pentane, hexane, heptane, cyclohexane, benzene, toluene, halogenated hydrocarbons such as methylene chloride and carbon tetrachloride as well as ethyl acetate and butyl acetate. The solution of the mono-isocyanates and the solvent is made such that the viscosity of the resulting solution is low enough to permit use with any form of application equipment. When using ethyl acetate, a preferred solvent, it has been found effective to employ a solution comprising 50% ethyl acetate and 50% octadecyl isocyanate, a preferred mono-isocyanate.

When mixing particulate soil with the mono-isocyanate either alone or in solution, it has been found that compositions having between 0.05% and 10% by weight isocyanate exhibit effective water-repellent characteristics. Especially effective and economical treated soils are those containing 1.5% to 2.5% isocyanates. Greater amounts are effective but are economically undesirable.

When spraying the isocyanate onto the surface of the soil or other porous silicious material 0.05 to 5, preferably 0.50 to 3, pounds of isocyanate per square yard of surface area has been found effective. Again greater amounts can be used but are economically undesirable.

The porous silicious materials which can be treated by the method of the present invention include among others cement, concrete, cinders, sand, soil, clay, pebbles and rocks. These materials may be in their naturally occuring form or may be formed into shapes such as bricks, building blocks, or walls and foundations of buildings. Particularly surprising and advantageous results are obtained when soil is treated with isocyanates in accordance with the present invention. Virtually any type of soil can be treated such as, for example, the various loams containing differing proportions of lime, sand, and clay, in addition to the usual decaying and decomposed vegetable and animal matter.

While it is not desired that the invention be limited to any theory, it appears that the isocyanates employed in the present invention react with any material in the soil having active hydrogen atoms, such as, for example, water, alcohols, amines, or polymers such as propoxylated glycol.

The present invention is further illustrated by the following examples which include a preferred embodiment. Unless otherwise indicated, all parts and percentages are by weight. Certain of the following examples employ a material called dry sand which is prepared by screening pure white silica sand through a #4 U.S. Standard sieve. That portion of the material which passes through a #4 sieve is air-dried. The water content is measured by well-known analytical methods and found to be less than 0.1%. Water is then added to this dry sand until the resultant composition has a water content of 10% based on the weight of sand. This material is termed moist sand and is typical of that which exists in the field and that which is employed in tests conducted by the Federal Government. This moist sand is thoroughly mixed and then placed in air-tight containers to equilibrate for at least 24 hours at the ambient temperature. At the end of that time, the soil is ready for use.

Example 1

A solution of 50 g. of octadecyl isocyanate and 50 g. of ethyl acetate was prepared. This solution was added in the following amounts to 100 g. samples of moist sand: 0.5, 1, 2, 4 and 10 g. of solution representing respectively 0.5, 1, 3 and 5 g. of octadecyl isocyanate. The solution and the moist sand were throughly mixed and left at room temperature for 2 hours. Water-repellency was then tested by placing a drop of approximately 0.05 cc. of water on the surface of the soil of each sample. The water soaked into the sample containing 1 g. of the solution. The drop of water on the sample containing 2 g. of solution wet the surface slightly. On all the remaining samples, the water droplets showed no tendency to spread or wet the soil either immediately after application or following a 10 minute interval.

Example 2

One hundred g. of dry sand were mixed with 6.2 g. (0.1 g. mole) of ethylene glycol. The following quantities of the octadecyl isocyanate were added to the ethylene glycol treated soil: 0.5, 1, 2, 5 and 10 g., the water-repellency noted was the same as that for the soil of Example 1.

Example 3

This example is not illustrative of the present invention but serves to clearly point out the ineffectiveness of certain diisocyanates as soil waterproofers.

One hundred g. samples of dry sand, sand containing 10% water, and sand containing 6.2 g. of ethylene glycol were mixed with 0.5, 1, 1.5, 2.5, 10, and 30 g. of hexamethylene diisocyanate. After two hours, the water-repellency of these samples was tested by placing a 0.05 cc. drop of water on the surface. In each case, the drop of water disappeared shortly after application, absorbed by the soil sample.

Example 4

The procedure of Example 3 was repeated with the single exception that diphenyl methylene diisocyanate replaced the hexamethylene diisocyanate. The results were the same as noted in Example 3, namely the drop of water disappeared shortly after application, absorbed by the soil sample.

Example 5

This example illustrates the construction of a road of naturally occurring soil by use of the method of the present invention.

A bulldozer is used to remove six inches of topsoil from two parallel roads or strips in an open, flat field. The roads are each 9 feet wide and 60 feet long (surface area=60 yd.^{2}) and have a 4 inch crown in the center. They are separated from one another by a 20 ft. strip of undisturbed material. The average water content of the soil comprising the surface of the two roads is measured by well-known analytical methods and found to be 8%.

A solution of 120 lb. of octadecyl isocyanate, 120 lb. of ethyl acetate and 1 lb. of dibutyl tin diacetate is prepared and subsequently sprayed evenly over one of the roads hereinafter termed the treated road, to give a uniform coverage of 2 lb. of isocyanate per square yard of road surface area. The second road remains untreated. The spraying process takes one hour.

Two hours after the spraying is completed the water repellency is tested by placing 10 drops of 0.05 cc. of water at various places on the treated and the untreated roads. All of the drops on the untreated road soak into the soil; only one drop on the treated road soaks in, the other nine drops remain on the surface.

One inch of rain in a 12 hour period two days after treatment plus vehicular traffic renders the untreated road muddy whereas the treated road remains firm and sheds water.

Many modifications of the present invention can be made, or will be apparent to those skilled in the art, without departing from the spirit and scope thereof.

What is claimed is:

1. A method for rendering porous silicious material water-repellent comprising the step of contacting the material with water-repelling amounts of a mono-isocyanate of the formula:

R—NCO

wherein R is a monovalent hydrocarbon radical of 6 to 32 carbon atoms.

2. The method of claim 1 wherein R is a monovalent aliphatic radical.

3. The method of claim 2 wherein R has 12 to 24 carbon atoms.

4. The method of claim 3 wherein the mono-isocyanate is octadecyl isocyanate.

5. The method of claim 4 wherein the octadecyl isocyanate is contacted with the porous silicious material as a mixture of:

(a) one to 99 weight percent isocyanate,

(b) one to 99 weight percent of an inert solvent, and

(c) catalytic amounts of dibutyl tin diacetate.

6. The method according to claim 1 comprising the additional step of treating the porous silicious material with a monomer having active hydrogen atoms.

7. The method according to claim 6, in which the monomer is an alcohol.

8. The method according to claim 6, in which the monomer is ethylene glycol.

9. The method according to claim 1 comprising the additional step of treating the soil with a polymer having active hydrogen atoms.

10. The method according to claim 9, in which the polymer is a member selected from the group consisting of polyols and polyamines.

11. The method according to claim 9, in which the polymer is propoxylated glycol.

12. The method according to claim 1 wherein the isocyanate is contacted with the surface of the porous silicious material in an amount equal to 0.05 to 5 pounds of isocyanate per square yard of surface area.

13. The method according to claim 12 wherein the isocyanate is contacted with the surface in an amount equal to 0.50 to 3 pounds of isocyanate per square yard of surface area.

14. The method of claim 1 wherein the porous silicious material is soil.

15. The method of claim 14 wherein the soil is in the form of a roadbed.

16. A composition of matter comprising:

(a) a porous silicious material, and

(b) water-repelling amounts of a mono-isocyanate of the formula:

$$R—NCO$$

wherein R is a monovalent hydrocarbon radical of 6 to 32 carbon atoms.

17. The composition of matter of claim 16 wherein R is a monovalent hydrocarbon radical.

18. The composition of matter of claim 17 wherein R has 12 to 24 carbon atoms.

19. The composition of matter of claim 18 wherein the isocyanate is octadecyl isocyanate.

20. The composition of matter of claim 16 wherein the porous silicious material is soil.

21. The composition of matter according to claim 16 further comprising a monomer having active hydrogen atoms.

22. The composition of matter according to claim 21, in which the monomer is an alcohol.

23. The composition of matter according to claim 21, in which the monomer is ethylene glycol.

24. The composition of matter according to claim 16 further comprising a polymer having active hydrogen atoms.

25. The composition of matter according to claim 24, in which the polymer is a member selected from the group consisting of polyols and polyamines.

26. The composition of matter according to claim 25, in which the polymer is propoxylated glycol.

27. A road constructed of the composition of matter of claim 16.

References Cited

UNITED STATES PATENTS

3,136,732	6/1964	Kaestner	94—22 X
3,141,304	7/1964	Moore	94—22 X

NILE C. BYERS, JR., *Primary Examiner.*